Supporting Information

Dinuclear copper(II) complexes of a polybenzimidazole ligand: their structures and induction roles in DNA condensation

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Experimental section

All chemicals were of reagent grade as received from commercial sources and used without further purification.

The ligand dtpb was prepared according to the earlier reported method.[1] And the ligand Bis(benzimidazol-2-yl-methyl)amine (IDB) was prepared according to the method described by Adams et al.[2]

Preparation of **1**. A clear blue methanol solution (20 mL) containing 0.2 mmol dtpb and 0.4 mmol $CuCl_2 \cdot 2H_2O$ after stirring for 2 h was obtained and left at room temperature without disturbing. Slow evaporation of solvents gave blue plate crystals of **2** (yield: 30%). Elemental analysis (%), calcd for $C_{46}H_{59}O_6N_{13}Cl_4Cu_2$: C47.64, H5.09, N15.70; found: C49.52, H4.70, N 16.65. IR data (cm^{-1}): 3390, 3055, 1621, 1593, 1452, 1275, 1078, 853, and 748.

Preparation of **2**. Crystals of **2** (0.05 mmol) and $Cu(NO_3)_2 \cdot 3H_2O$ (0.1 mmol) were dissolved in methanol (10 mL) and stirred for 30 min. The resulting clear blue solution was left at room temperature without disturbing. Slow evaporation of solvents gave blue plate crystals of **3** (yield: 40%). Elemental analysis (%), calcd for $C_{46}H_{55}Cl_2Cu_2N_{15}O_{10}$: C46.94, H4.77, N17.86; found: C47.50, H4.28, N18.85. IR data (cm^{-1}): 3066, 1623, 1553, 1390, 1363, 1286, 1052, 823, and 748.

Preparation of $[Cu(idb)Cl_2]CH_3OH$. This complex was synthesized by reaction of IDB (0.2mmol) and 0.2 mmol $CuCl_2 \cdot 2H_2O$ in 30ml methanol solution at 333 K for 2 h. The resulting solution was filtered and blue block crystals

suitable for X-ray diffraction were obtained by slow evaporation of the filtrate at room temperature overnight (yield: 30%). Elemental analysis (%), calcd for $C_{17}H_{19}Cl_2CuN_5O$: C 46.01, H 4.31, N 15.78; found: C45.98, H4.43, N15.72. IR data (cm^{-1}): 3364, 3065, 1659, 1573, 1400, 1109, 727 and 627.

Physical measurments

C, H, N elemental analysis was performed on a Vario EL III elemental analyzer. The infrared spectrum was recorded on KBr pellets with a NEXUS470–IR spectrometer in the range of 400–4000 cm^{-1}.

All the data were collected on a Nonius Kappa CCD diffractometer with Mo *Ka* radiation (λ = 0.71073 Å). Empirical absorption corrections were applied using the multi-scan program. The structures were solved by direct (or patterson) methods and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms with the SHELX-97 program.[3,4] For compounds 1-3, all of the non-hydrogen atoms (except for some solvent molecules in some cases) were refined with anisotropic thermal motion parameters, and the contribution of the hydrogen atoms was included in calculated positions.

For dtpb, O1w was located at the special position of the inversion center and O5w was refined with its occupancy constrained to be 0.5. Owing to the serious crystal deterioration, although the crystals selected were sealed in capillaries with mother liquid, some of the non-coordinated solvent molecules could not be modeled by discrete atoms in **1** and **2**. The contribution of the solvent to the diffraction pattern was subtracted using the SQUEEZE procedure of PLATON (Spek, 2003).[5]

For **1**, five water and two methanol molecules have been determined during the structural refinement. The contributions of the rest solvent molecules are subtracted using SQUEEZE procedure. The voids are 901.1 $Å^3$ per unit cell (consisted of about 8.17% percent of the crystal volume, equally distributed across four cavities), corresponding to additional 5~6 H_2O molecules. A similar treatment was performed in refinement of **2**. The voids (626 $Å^3$) were found and additional 7~8 water molecules should be included in each coordination compound molecule. In both 1 and 2, the hydrogen atoms bonded to solvent molecules are not fully positioned. Owing to the serious disorder of the solvent molecules, some short intermolecular contacts have been caused in the CheckCIF report. These contacts should be omitted.

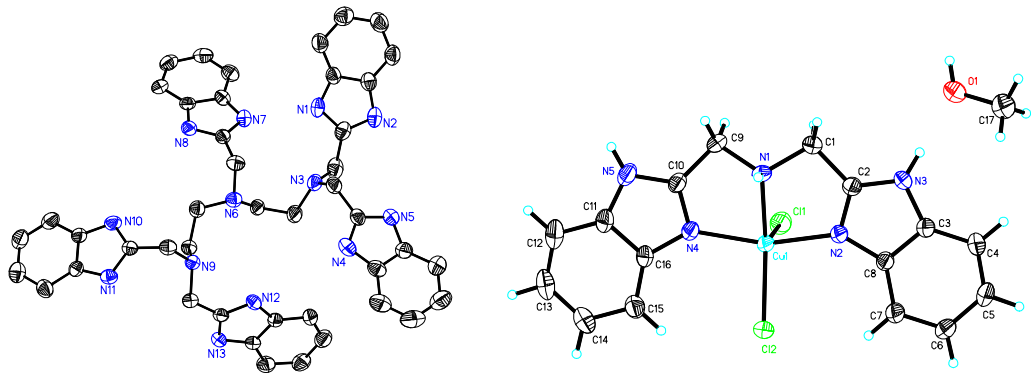
For $[Cu(idb)Cl_2]CH_3OH$, the aimine N atom was disordered over two positions. The final occupancies for the major and minor components are 0.54(1) and 0.46(1), respectively. H atoms bonded to C atoms were located at the geometrical positions and H atoms bonded to N and O atoms were found from the difference maps with the constraints of N-H=0.86(1)Å and O-H=0.82(1)Å.

Table S1. Crystal parameters of dtpb and mono- and dinuclear Cu(II) complexes

	1	2	dtpb	$[Cu(idb)Cl_2]CH_3OH$
empirical formula	$(C_{44}H_{43}Cl_2Cu_2N_{13})\cdot(H_2O)_4\cdot(CH_3OH)_2\cdot Cl_2$	$(C_{44}H_{45}Cl_2Cu_2N_{13}O)\cdot(CH_3OH)_2\cdot(NO3)_2\cdot H_2O$	$(C_{44}H_{43}N_{13})\cdot(H_2O)_{3.5}$	$(C_{16}H_{15}Cl_2CuN_5)\cdot(CH_3OH)$
Formula weight	1158.85	1176.01	825.97	443.81
Crystal system	Monoclinic	Triclinic	Orthorhombic	Orthorhombic
Space group	*C*2/c	*P*-1	$C222_1$	*P b c a*
Unit cell dimensions				
a (Å)	28.1248(16)	13.6420(6)	8.3956(5)	14.0278(3)
b (Å)	20.2139(10)	15.0146(6)	29.5409(18)	14.3718(3)
c (Å)	19.4855(10)	16.3045(7)	35.872(2)	18.2724(5)
α (°)	90	70.145(1)	90	90
β (°)	95.672(1)	86.293(1)	90	90
γ (°)	90	81.483(1)	90	90
Volume ($Å^3$)	11023.5(10)	3106.1(4)	8896.8(9)	3683.80(15)
Z	8	2	8	8
Calculated density (Mg/m^3)	1.383	1.255	1.232	1.600
F(000)	4712	1212	3496	1816
Crystal size	0.20×0.1 0×0.06	0.20×0.10×0.10	0.30×0.20×0.20	0.23 ×0.16 × 0.10
θ range (°)	1.58-25.00	1.95-25.00	1.49-25.00	2.23-28.28
Reflections collected	48636	29442	25509	40793
Independent reflections	9675	10724	4328	4492
Number of parameters	613	692	555	261
Goof %	1.082	0.916	0.891	0.980
Final R indices [I>2σ(I)]	R_1=0.0716 WR_2=0.1772	R_1=0.0782 WR_2=0.2172	R_1=0.0581 WR_2=0.1302	R_1=0.0463 WR_2=0.1215
R indices (all data)	R_1=0.1503 WR_2=0.2029	R_1=0.1136 WR_2=0.2374	R_1=0.099 WR_2= 0.1418	R_1=0.0724 WR_2=0.1286
Largest diff. peak and hole($eÅ^{-3}$)	0.878, -0.596	0.963, -0.475	0.337, -0.300	0.942, -0.733

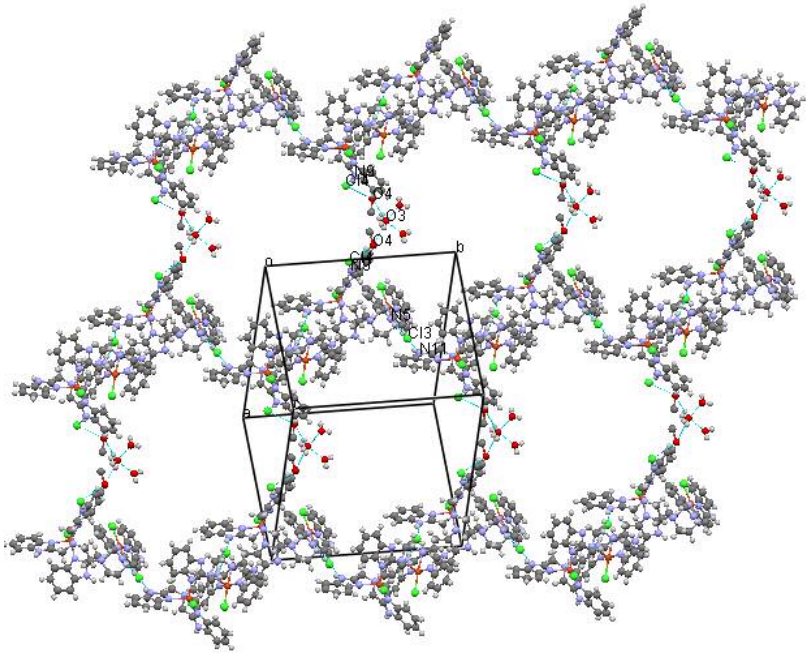
Table S2. Selected bond lengths (Å) and angles (°) data for 1, 2 and $[Cu(idb)Cl_2]CH_3OH$.

1		2		$[Cu(idb)Cl_2]CH_3OH$	
Bond distances					
Cu1-N2	2.515(5)	Cu1-N1	2.506(3)	Cu1-N1	2.031(8)
Cu1-N1	2.130(5)	Cu1-N3	2.124(4)	Cu1-N2	1.985(3)
Cu1-N6	1.966(5)	Cu1-N11	1.965(5)	Cu1-N4	1.990(4)
Cu1-N4	1.973(6)	Cu1-N13	1.956(4)	Cu1-Cl1	2.602(2)
Cu1-Cl1	2.241(2)	Cu1-Cl1	2.239(1)	Cu1-Cl2	2.267(1)
Cu2-N8	1.982(5)	Cu2-N2	2.200(4)		
Cu2-N10	2.145(5)	Cu2-N7	1.950(4)		
Cu2-N12	1.990(5)	Cu2-N9	1.931(4)		
Cu2-N3	2.300(4)	Cu2-Cl2	2.329(2)		
Cu2-Cl2	2.278(2)	Cu2-O1	2.390(4)		
Bond angles					
N1-Cu1-N2	80.88(14)	N1-Cu1-N3	81.72(14)	N1-Cu1-N2	80.0(3)
N2-Cu1-N6	88.03(18)	N1-Cu1-N11	93.12(14)	N1-Cu1-N4	79.2(3)
N2-Cu1-N4	101.29(14)	N1-Cu1-N13	100.71(14)	N1-Cu1-Cl1	103.6(7)
N2-Cu1-Cl1	104.58(14)	N1-Cu1-Cl1	99.00(12)	N1-Cu1-Cl2	156.0(7)
N1-Cu1-N6	81.9(2)	N3-Cu1-N11	82.99(19)	N2-Cu1-N4	158.83(16)
N1-Cu1-N4	80.8(2)	N3-Cu1-N13	81.09(17)	N2-Cu1-Cl1	93.97(12)
N1-Cu1-Cl1	174.54(14)	N3-Cu1-Cl1	178.83(13)	N2-Cu1-Cl2	98.94(11)
N4-Cu1-N6	158.8(2)	N11-Cu1-N13	157.11(11)	N4-Cu1-Cl1	94.95(12)
N6-Cu1-Cl1	97.96(16)	N11-Cu1-Cl1	97.88(15)	N4-Cu1-Cl2	98.28(11)
N4-Cu1-Cl1	98.02(17)	N13-Cu1-Cl1	97.86(12)	Cl1-Cu1-Cl2	100.40(6)
N3-Cu2-N8	78.42(18)	N2-Cu2-N7	79.79(17)		
N3-Cu2-N10	75.89(17)	N2-Cu2-N9	81.98(18)		
N3-Cu2-N12	93.56(18)	N2-Cu2-O1	118.68(16)		
N3-Cu2-Cl2	172.11(13)	N2-Cu2-Cl2	151.40(14)		
N8-Cu2-N10	114.4(2)	N7-Cu2-N9	158.8(2)		
N8-Cu2-N12	142.7(2)	N7-Cu2-O1	100.8(2)		
N8-Cu2-Cl2	96.02(14)	N7-Cu2-Cl2	94.95(14)		
N10-Cu2-N12	98.30(19)	N9-Cu2-O1	96.25(17)		
N10-Cu2-Cl2	101.73(14)	N9-Cu2-Cl2	97.66(15)		
N12-Cu2-Cl2	94.24(14)	O1-Cu2-Cl2	89.90(13)		

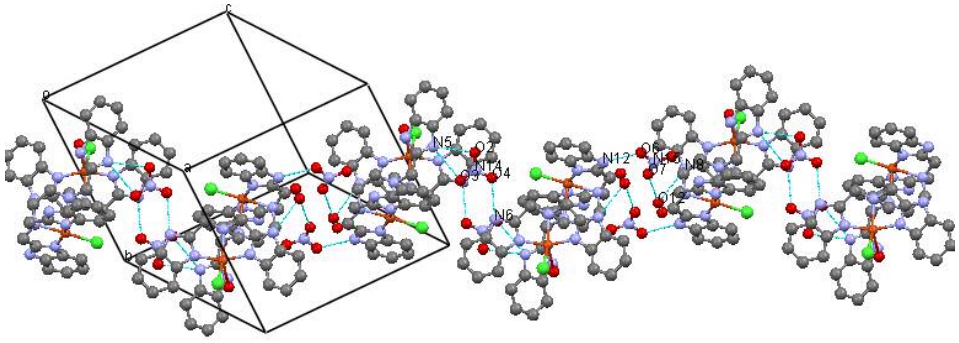


(a) (b)

Figure S1. ORTEP view of the ligand dtpb (**a**) and [Cu(idb)Cl_2]CH_3OH (**b**). For clarity, solvent molecules and hydrogen atoms are omitted.



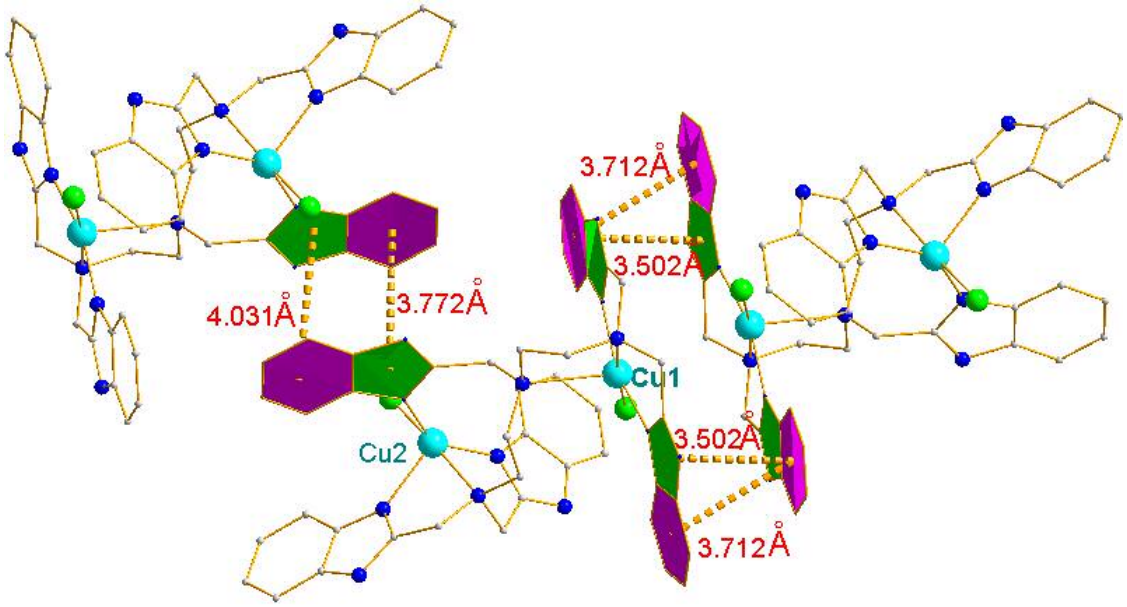
(a)



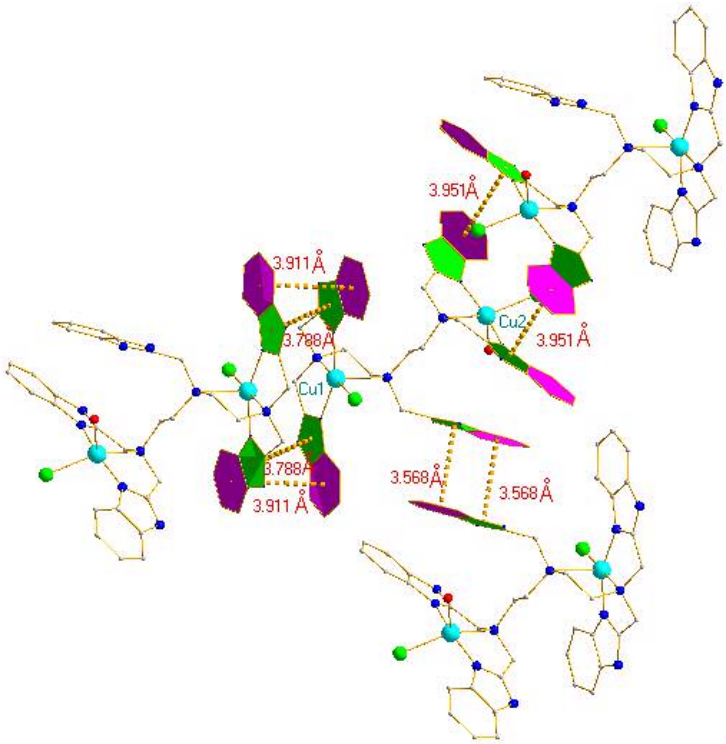
(b)

Figure S2. (**a**) Showing the formation of the 2-D hydrogen bond network in **1** by the combinative actions of N9…Cl4…O4…O3…O4…Cl4…N9A and N5…Cl3…N11 hydrogen bonded linkages, some solvent molecules not involved in the motif have been omitted for clarity;

(**b**) Showing the formation of the one-dimensional chains in **2** by the combinative actions of N5…O2/O3-N14-O4…N6 and N8…O12…O7-N15-O6…N12 hydrogen bonded linkages, some solvent molecules not involved in the motif have been omitted for clarity.



(a)



(b)

Figure S3. Showing the π-π stacking interactions in **1** (**a**) and **2** (**b**). For clarity, solvent molecules, hydrogen atoms and counter anions are omitted. The distances between these symmetry-related centroids are labeled besides the dashed lines.

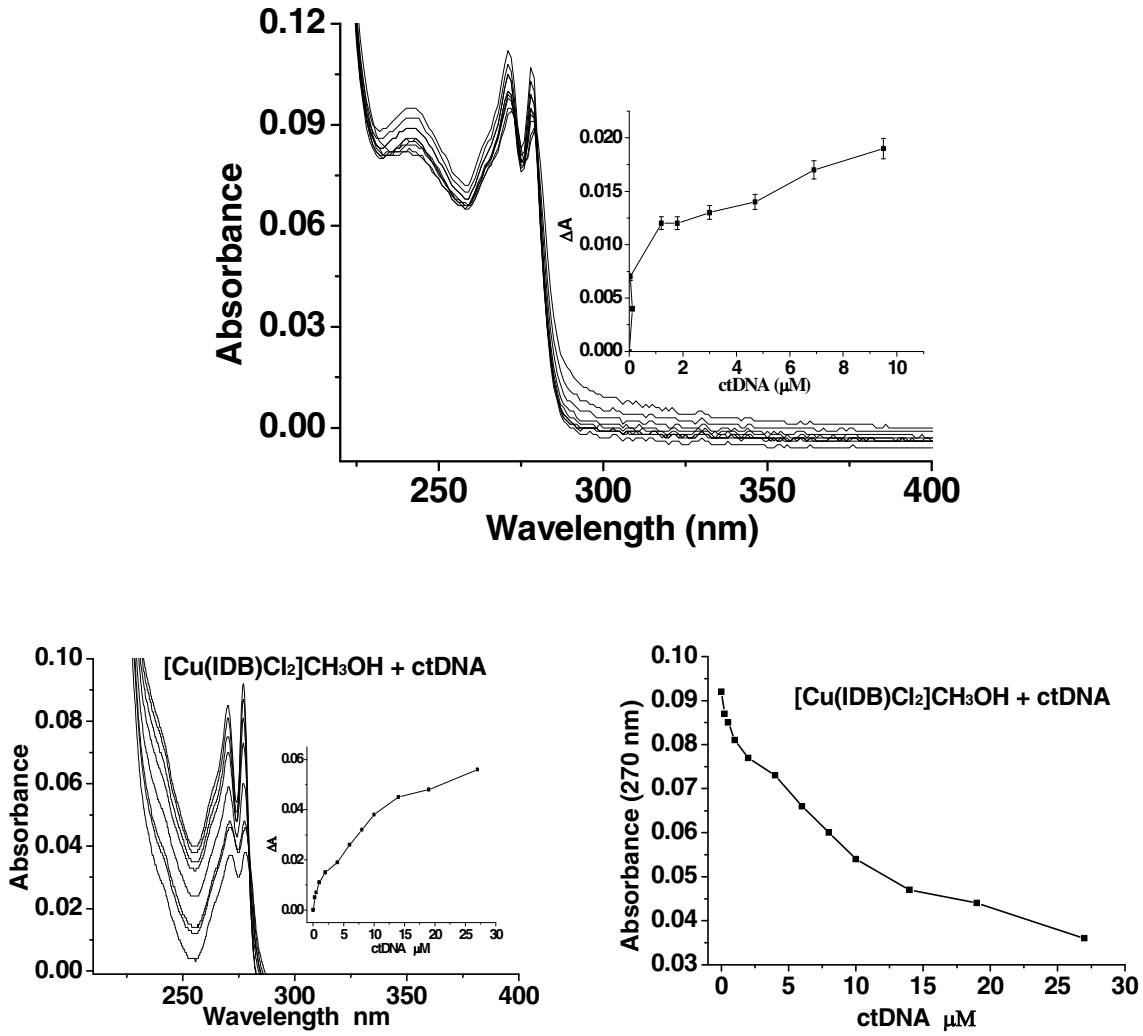


Figure S4. Titration of **1** (4 μM, upper), **2** (4 μM, middle) and $[Cu(idb)Cl_2]CH_3OH$ (20 μM, bottom right and left) with calf thymus DNA (ctDNA, 0–11.10 μM in base pairs) monitored by UV-visible absorption spectra. The mixtures of **1**, **2** or $[Cu(idb)Cl_2]CH_3OH$ with ctDNA were incubated for 3 min at 37 ^oC in 20 mM Tris-HCl buffer (pH 7.4) prior to measurement. The apparent binding equilibrium constants of each complex to ctDNA were obtained by fitting the changes in absorbance values at 270 nm (ΔA) with the concentration of each complex (inset) to a previously proposed model.[6]

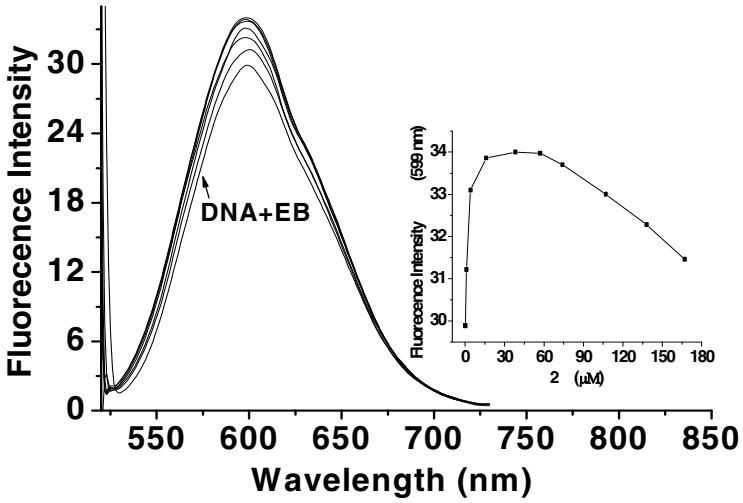


Figure S5. Changes in the fluorescence spectra of (EtBr, excitement wavelength 510 nm) intercalated into ctDNA with concentration of **1**. The complex **1** was increasingly added into the mixture containing ctDNA and EtBr (1:1 for base pair:EtBr) and incubated for 60 s at 37 ^{o}C in 20 mM Tris-HCl buffer (pH 7.4) prior to measurement. Addition of **1** (< 45 μM) leads to DNA condensation and more extensive hydrophobic circumstance around EtBr. Thus, the emission intensity of EtBr was first enhanced (inset). Further addition of **1** (> 45 μM) causes exclusion of EtBr from the interior of DNA double strands, thereby emission intensity of EtBr being reduced. Here, ΔF is the changes in the fluorescence intensity at 599 nm of EtBr intercalated into ctDNA with concentration of **1**, as shown in the inset.[7]

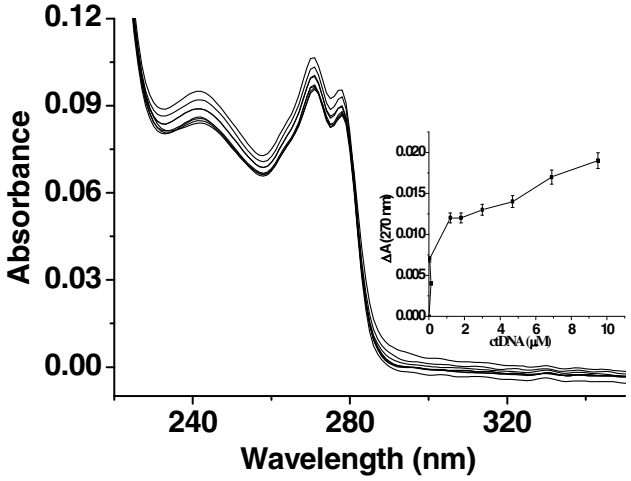


Figure S6. Changes in the absorption spectra of **1** with ctDNA concentration. The mixtures of **1** with ctDNA of increasing concentration were incubated for 60 s at 37 ^{o}C in 20 mM Tris-HCl buffer (pH 7.4) prior to measurement. Here, ΔA is the changes in absorbance at 270 nm of **1** with concentration of ctDNA, as shown in the inset.

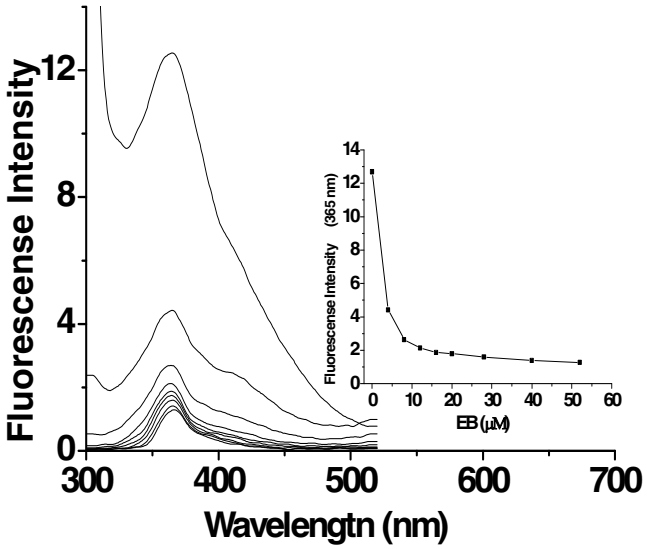


Figure S7. Changes in the fluorescence spectra of **1** (excitement wavelength 270 nm) bound to ctDNA with concentration of EtBr. EtBr was increasingly added into the mixture of ctDNA with **1** (1:1 for base pair: EtBr) and incubated for 60 s at 37 ^{o}C in 20 mM Tris-HCl buffer (pH 7.4) prior to measurement. The fluorescence intensity of **1** was progressively reduced upon addition of EtBr. Here, ΔF is the changes in the fluorescence intensity at 365 nm of **1** bound to ctDNA with concentration of EtBr, as shown in the inset.

References:

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